

Water Soluble Branched Block Copolymers

5 The invention pertains to water soluble branched block copolymers comprising quaternary ammonium compounds and poly(alkylene glycols), whereby the molecular building blocks, which contain the quaternary ammonium groups, form backbone chains that are linked together in a wide mesh manner via poly(alkylene glycol) blocks.

10 Water soluble cationic polymers and copolymers are of great practical importance. They are used as coagulating agents and flocculating agents in many industrial processes in which suspended solids have to be separated out of aqueous systems. Typical examples are the paper manufacturing process, the separation of interfering substances in closed water circuits, and the processes for waste water
15 treatment and the removal of water from sludge for the purification of communal and industrial waste water.

The effectiveness of a water soluble cationic polymer as a coagulating and flocculating agent depends, in essence, on the following parameters: the nature of the
20 selected monomers, the molecular weight of the polymer, and the architecture of the polymer chain.

Diallylammonium compounds have found broad application as monomers because of their hydrolytic stability and their general chemical stability.
25 Poly(diallyldimethylammonium chloride) (poly-DADMAC), in particular, excels by virtue of its superb long-term stability. The radical polymerization of monomeric DADMAC leads to linear polymer structures (US 3,288,770 and DD 127 729).

Their efficacy for use as coagulating agents and flocculating agents
30 depends on the molecular weight of the polymers. An increase in their molecular weight has therefore been striven for on many occasions. In order to do this, US 4,713,431 describes a polymerization process for DADMAC using the inverse emulsion procedure instead of polymerization in aqueous solution. An increase in molecular weight can also be achieved via the radical copolymerization of DADMAC with polyfunctional
35 crosslinking comonomers in aqueous solution, whereby branched and/or crosslinked structures are formed. Bisallyl esters of dicarboxylic acids (DD 127 729, DD 128 189, D

128 247, DE 27 38 758) and triallylammonium compounds and tetraallylammonium compounds (FR 1494 438, US 3,544,318, WO 99/13155 and WO 99/19262) have been proposed as chain lengthening comonomers. The copolymerization of DADMAC using the inverse emulsion procedure with triallylammonium salts or tetraallylammonium salts or methylenebisacrylamide is described in US 3,968,037. Small quantities of branching agents are generally added at the beginning of polymerization.

It is well known that the resulting polymer is already partially or completely crosslinked at a concentration of the polyfunctional comonomers in excess of 0.1 %. This leads to the formation of gel fractions all the way through to complete insolubility of the polymer in the solvent (Vollmert, Grundriss der Makromolekularen Chemie ["Outline of Macromolecular Chemistry"], Springer-Verlag, Berlin, 1962, page 196).

An improved process is present if the polyfunctional comonomer is metered in, either step-wise or continuously, during polymerization (EP 0 264 710). The comonomer can now be incorporated to a greater extent, and polymers are generated with a higher molecular weight. However, a rather complicated addition program is required, and the risk of gel formation can only be reduced, but not ruled out. Moreover, the aspect cannot be avoided that macromolecules with a low degree of polymerization are also produced along side highly branched polymer chains with a high molecular weight. This fraction with a low molecular weight is disadvantageous because of its low efficiency in use. Water soluble cationic polymers, which are prepared with polyfunctional crosslinking comonomers, have a higher molecular weight than polymers that have been prepared without these comonomers. However, their properties in terms of usage are not yet optimal because they exhibit a very narrow mesh network with a poor state in solution. This is seen on the basis of measured values of the solution viscosimetry in aqueous salt solutions. These give rise to low intrinsic viscosities and high Huggins constants.

Branched water soluble cationic polymers can also be prepared by means of graft copolymerization. Thus the radical grafting of DADMAC/acrylamide mixtures is carried out on a pre-polymer comprising DADMAC and dihydroxyalkyl derivatives of acrylic acid by means of initiation via cerium(IV) salts (G.B. Butler, J. Macromol. Sci., A 26 (1989) page 681). However, high concentrations of the prepolymer are required in

this connection and polymer yields of [only] approximately 80 % are obtained which is industrially unsatisfactory. An additional process describes the copolymerization of acrylamide with macromonomers of cationic compounds in order to prepare branched cationic polymers (US 5,211,854). This process is economically unfavorable, however.

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Branched poly(ammonium salts) can be prepared in a two-stage process in accordance with the data of DE 195 24 867. The synthesis of a prepolymer, which contains amine groups, takes place first of all. Graft polymerization with DADMAC as the cationic monomer is then started via redox initiation at the amine groups, and thus the branched structure is built up. Comb-like cationic copolymers are formed with molecular weights of more than 100,000 g/mol, and preferably more than 250,000 g/mol. The intrinsic viscosities are between 0.68 and 1.37 dl/g. Typical values for the Huggins constants of products, which have been prepared in accordance with DE 195 24 867, are in excess of 0.6, and are distinctly above the values of 0.3 to 0.5 that are characteristic of a good state in solution.

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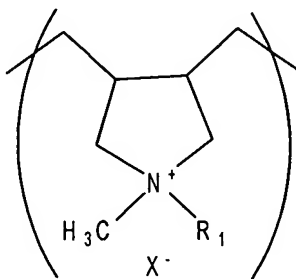
Proceeding on the basis of this, the problem for the present invention was to eliminate the designated disadvantages of the prior art, and to make available water soluble cationic block copolymers with a branched structure with a high molar mass and a good state in solution.

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This problem is solved by block copolymers with the features of claim 1 and the process for their preparation with the features of claim 9. The additional dependent claims indicate advantageous further developments. The use of the block copolymers in accordance with the invention is described in claims 17 and 18.

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In accordance with the invention, water soluble branched block copolymers comprising quaternary ammonium units of general formula I



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In contrast to the previously known highly cationic polymers, the poly(ammonium salts), which are branched in a wide mesh manner, exhibit better properties in a series of usage sectors: in general, improved but at least comparable separating effects are achieved with a reduced quantity of the additive that is used, especially in the removal of water from industrial and communal sludges. In comparison to conventional commercial products, distinctly improved values have been achieved in the kaolin sedimentation test in regard to the parameters relating to deposition velocity and residual turbidity. Similarly good results have also been achieved in the CST test using putrefying communal sludges. The CST values here are many times better than commercial reference products, especially in the case of a very low dosage. Noteworthy results have also been achieved with industrial sludges (waste water sludge from the manufacture of paper), where particularly superb values for flocculate formation and water removal properties are to be emphasized.

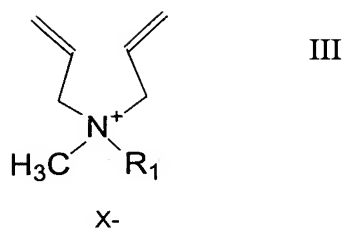
The new polymers have controllably adjustable molecular weights and intrinsic viscosities. The molecular weights are preferably in excess of 250,000 g/mol, and especially preferably in excess of 1,000,000 g/mol. The intrinsic viscosities are adjustable between 25 and 600 ml/g, and they preferably lie between 400 and 600 ml/g. The Huggins constants are preferably between 0.3 and 0.5.

The quaternary ammonium unit is preferably derived from diallyldimethylammonium chloride (DADMAC).

The poly(alkylene glycol) blocks are preferably derived from compounds from the group of bis-acrylate esters or bis-methacrylate esters of poly(ethylene glycols), poly(propylene glycols), poly(butylene glycols), and/or polytetrahydrofurans.

Chloride or methosulfate is preferably present as a suitable counterion X^- .

A process is made available in accordance with the invention for the preparation of water soluble branched block copolymers via the radical polymerization of a quaternary diallylammonium compound of general formula III,



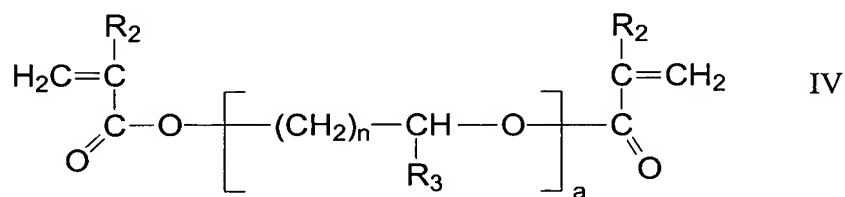
with

$R_1 = \text{H, alkyl (C}_1\text{-C}_8\text{)}$

5 $X^- = \text{a suitable counterion,}$

and a bis-acrylate ester or a bis-methacrylate ester of a poly(alkylene glycol) of general formula IV,

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with

$R_2 = \text{H, methyl,}$

15 $R_3 = \text{H, methyl, ethyl,}$

$X^- = \text{a suitable counterion,}$

$n = 1 \text{ through } 3 \text{ independently of one another,}$

$a = 6 \text{ through } 100,$

20 in the same way. The proportion by mass of the compound of general formula IV is hereby between 0.01 and 20 % by weight based on the two starting compounds.

Polymerization can be started with any desired water soluble initiators, such as azo compounds or redox systems comprising persulfate and amines.

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Polymerization can also take place in aqueous solution or, preferably, using the inverse emulsion procedure. The addition of the bis-acrylate ester or bis-methacrylate ester of the poly(alkylene glycol) takes place in the 0 to 80 % range of extents of reaction either in the form of one shot, or in portions, or continuously.

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The block copolymers find use as coagulating agents and flocculating agents in many industrial processes in which suspended solids have to be separated out of aqueous systems. Typical examples are the process for the manufacture of paper, the separation of interfering substances in closed water circuits, and the processes for the treatment of waste water and the removal of water from sludge for the purification of communal and industrial waste water.

The subject in accordance with the invention will be elucidated in more detail by means of the following examples that pertain to the polymerization of DADMAC as a typical cationic monomer. However, the examples are not to be considered as being a limitation representing the sole use of this monomer for the present invention.

Example 1

The oil phase, which comprises a mixture of 240 g of Isopar M (Exxon), 8 g of Span 80 (ICI), 8 g of Hypermer 1599 D (ICI), 8 g of Tween 85 (ICI), and 8 g of NXC 3 (Condea), is introduced into a 1 liter glass reactor, which is capable of being thermostatically regulated and which is equipped with an anchor-shaped stirrer and a gas inlet line, and the separately prepared aqueous phase is metered in over a period of 10 minutes with stirring at 200 min^{-1} . The composition of the aqueous phase, which is adjusted to pH 4 with HCl, is given by the following components:

- 502 g of DADMAC (62 %),
- 1.2 g of poly(ethylene glycol) dimethacrylate (molecular weight approximately 875 g/mol),
- 65 g of 1 % EDTA solution.

The emulsion that is produced is thermostatically regulated to 45°C , and purged with nitrogen for 30 minutes. A solution of 1.6 g of V-65 (2,2'-azobis-(2,4-dimethylvaleronitrile)) dissolved in 10 ml of toluene is then metered into the emulsion over a period of 2 hours. After a further reaction time of 2 hours, the temperature is raised to 65°C , and an addition is made of a further 300 mg of V-65 dissolved in 5 ml of toluene. The reaction mixture is held for a further 3 hours at this temperature. The

gravimetric determination of the extent of reaction via precipitation in acetone and re-precipitation with use being made of methanol as the solvent resulted in an extent of reaction of 96 %. The material properties were characterized by determining the limiting viscosity index via an evaluation in 1 N NaCl solution. In accordance with the Huggins method. $[\eta]$ was determined to be $221 \text{ cm}^3/\text{g}$ for the product, and the corresponding Huggins constant was 0.37.

Example 2

10 Reference example without crosslinking agents

The polymerization experiment in accordance with example 1 is repeated, but without a crosslinking component and, by contrast, 16 g of 50 % acrylamide are additionally added to the aqueous phase. The experiment resulted in an extent of polymerization of 97 %. A limiting viscosity index of $135 \text{ cm}^3/\text{g}$ was determined for the isolated product, and the k_H value was 0.39.

Examples 3 and 4

20 An oil phase comprising 240 g of Isopar M (Exxon), 6 g of Span 80 (ICI), 8 g of Hypermer 1599 D (ICI), 8 g of Tween 85 (ICI), and 10 g of NXC 3 (Condea) is prepared and transferred to the stirred reactor. The more hydrophobic crosslinking agents that are used in examples 3 and 4 that are described here - rather than the crosslinking agent on the basis of poly(ethylene glycol) from example 1 - namely
25 poly(propylene glycol) bisacrylate (1.2 g; molecular weight approximately 900 g/mol) for example 3, and polytetrahydrofuran bismethacrylate (2.6 g; molecular weight approximately 2000 g/mol) for example 4, are added to the oil phase, whereby the temperature is simultaneously raised to 50°C , and the solution is purged with nitrogen for 30 minutes. The quantities of crosslinking agents that are used correspond in each
30 case to equimolar ratios (0.7 mmol/mol of monomer in each case). The separately prepared aqueous phase comprising 502 g of DADMAC (62 %) and 65 g of 1 % EDTA solution (a solution with the pH adjusted to 4 with HCl) is dispersed in the oil phase using a rate of stirring of 150 min^{-1} . Use is made of V-60 (AIBN, 2,2'-azobisisobutyronitrile) in order to initiate polymerization. 1.5 g of the initiator, dissolved
35 in 10 ml of toluene, are metered in over a period of 2 hours. The reaction mixture is then

held at this temperature for 2 hours before being heated to 60 °C. 0.7 g of AIBN in 10 ml of toluene is then added in the form of one shot, and the reaction mixture is held for a further 2 hours at this temperature. The values that are achieved for the extent of reaction for the examples in question were 95.5 % for example 3, and 96 % for example 4. The limiting viscosity index was 254 cm³/g ($k_H = 0.42$) for the product from example 3, and 185 cm³/g ($k_H = 0.38$) for the product from example 4.

Example 5

The mixing conditions and the implementation of the reaction correspond to example 1. However, EDTA is used in the form of a 5 % solution together with three times the quantity of the crosslinking agent. The crosslinking agent is dissolved in 30 ml of water and metered continuously into the reaction mixture over a period of 5.5 hours. The test sample for determining the extent of reaction resulted in a final extent of reaction of 98 %. A limiting viscosity index of 585 cm³/g was ascertained, whereby a Huggins constant of 0.44 resulted.

Examples 6 and 7

The effect on the polymer properties of a polymeric and a structurally similar low molecular weight crosslinking agent are described as a reference example. The method of working is again in accordance with the basic process in accordance with example 1, whereby use is made of poly(ethylene glycol) diacrylate (1.0 g; molecular weight approximately 700 g/mol) in example 6, and ethylene glycol diacrylate (250 mg) in example 7. The extent of reaction of the two examples amounted to 97 % at the end in each case; the limiting viscosity index in 1 N NaCl solution was determined to be 280 cm³/g for the product from example 6, whereby a value of $k_H = 0.39$ resulted. By contrast, a limiting viscosity index of 185 cm³/g and a Huggins constant of 0.94 were measured for the product from example 7.

Examples 8 through 14

Usage test: kaolin sedimentation (KSD)

Samples from examples 1, 5, and 6 were examined in terms of KSD activity in comparison to the samples from example 2 (without crosslinking agents), and

7 (low molecular weight crosslinking agent), and high molecular weight branched chain samples in accordance with example 2 of WO 99/13155 (polymer 16), and example 1 of DE 195 24 867. In order to do this, the high molecular weight reference samples were prepared in accordance with the recipes that are disclosed in the respective patent specifications, and all the samples were prepared in the form of 1 % solutions following phase inversion. 5 ppm of the polyelectrolyte solutions were in each case added with stirring to freshly prepared 2 % kaolin suspensions. After an additional 5 minutes of stirring, the stirrer was stopped, and the onset of, and the course taken by, the sedimentation process were determined along with the residual turbidity via light transmission measurements. The values that were determined are contained in Table 1.

Table 1

Example	Sample	Onset of sedimentation [s]	Rate of sedimentation [cm/s]	Residual turbidity [%]
8	product from example 1	18	0.24	8.1
9	product from example 5	14	0.19	7.5
10	product from example 6	21	0.24	10.0
11	product from example 2	37	0.34	27
12	product from example 7	28	0.28	23.2
13	DE 195 24 867 (example 1)	26.5	0.29	20.7
14	WO 99/13155 (polymer 16)	24	0.27	22

5 The measurements show that the sample in accordance with example 5 is the most effective sample. A direct comparison of the products that were [verb omitted] on the one hand with a polymeric crosslinking agent (example 10 - product from example 6) and, on the other hand, with a structurally related low molecular weight crosslinking agent (example 12 - product from example 7) unambiguously shows the superiority in this usage test of the polymers that were branched in a wide mesh manner as a result of using polymeric crosslinking agents.

Examples 15 through 21

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The same samples, which were used for the KSD tests, were examined in terms of their efficacy for removing water from sludge. CST measurements took place in order to do this. In each case, 250 ml of putrefying sludge were sheared at 800 revolutions [per unit time] for this purpose. The polyelectrolytes were again prepared in the form of 1 % solutions following phase inversion. The CST values were determined 15, 30, and 60 seconds after the addition of polymer (the usual addition of 200 ppm has been selected here as an example) to the sheared putrefying sludge. Table 2 contains the results that were determined from the measurements.

Table 2

Example	Sample	CST value after		
		15 s	30 s	60 s
15	product from example 1	10	12	13
16	product from example 5	9	10	10
17	product from example 6	11	13	14
18	product from example 2	32	35	44
19	product from example 7	19	21	29
20	WO 99/13155 (polymer 16)	14	17	19
21	DE 195 24 867 (example 1)	11	14	15

The product from example 5 above proves to be the most effective in this test as well.